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(72) NABER, Bernhard, DE

(72) GASSAN, Michael, DE

(72) HENDREICH, Regina, DE

(72) NEISS, Vera, DE

(71) BASF Aktiengesellschaft, DE

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(54) **PRODUCTION DE MOUSSES INTEGREES DE**

POLYURETHANE, POSSEDANT UNE RESISTANCE

AMELIOREE A LA PROPAGATION DE LA DECHIRURE ET A

L'ELONGATION A LA RUPTURE, AINSI QU'UNE

MEILLEURE RESISTANCE A LA TRACTION

(54) **PRODUCTION OF TOUGH POLYURETHANE INTEGRAL**

FOAMS HAVING IMPROVED TEAR PROPAGATION

RESISTANCE, ELONGATION AT BREAK AND TENSILE

STRENGTH

(57) Mousse intégrée de polyuréthane possédant une résistance améliorée à la propagation de la déchirure, à l'élongation à la rupture et une meilleure résistance à la traction; elles sont produites par réaction a) de polyisocyanates organiques et (ou) organiques modifiés avec b) au moins un composé de masse molaire relativement élevée, contenant au moins deux atomes d'hydrogène réactifs et, si souhaités c) des extenseurs de chaîne, de faible masse molaire, et (ou) des réticulants en présence de d) catalyseurs e) si souhaités, des agents d'expansion, f) et, si souhaités, d'autres agents d'appoint et (ou) additifs; le constituant b utilisé renferme au moins un polyol recyclé, obtenu par glycolyse de mousses intégrées de polyuréthane résistantes avec des éthers glycidiques. Les mousses obtenues par le présent procédé peuvent servir comme revêtement pour des barils de bière.

(57) Tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength are produced by reacting a) organic and/or modified organic polyisocyanates with b) at least one relatively high molecular weight compound containing at least two reactive hydrogen atoms and, if desired, c) low molecular weight chain extenders and/or crosslinkers in the presence of d) catalysts, e) if desired, blowing agents f) and also, if desired, further auxiliaries and/or additives, wherein the component b) used comprises at least one recycled polyol which is obtained by glycolysis of tough polyurethane integral foams using glycidyl ethers. The tough polyurethane integral foams produced by this process can be used as beer barrel cladding.



Production of tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength

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Abstract

Tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength
10 are produced by reacting

- a) organic and/or modified organic polyisocyanates with
 - 15 b) at least one relatively high molecular weight compound containing at least two reactive hydrogen atoms and, if desired,
 - c) low molecular weight chain extenders and/or crosslinkers
 - 20 in the presence of
 - d) catalysts,
 - e) if desired, blowing agents
 - 25 f) and also, if desired, further auxiliaries and/or additives,
- wherein the component b) used comprises at least one recycled polyol which is obtained by glycolysis of tough polyurethane
30 integral foams using glycidyl ethers. "

The tough polyurethane integral foams produced by this process can be used as beer barrel cladding.

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Production of tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength

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The present invention relates to a process for producing tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength by reacting

10 a) organic and/or modified organic polyisocyanates with

b) at least one relatively high molecular weight compound containing at least two reactive hydrogen atoms and, if desired,

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c) low molecular weight chain extenders and/or crosslinkers

in the presence of

20 d) catalysts,

e) if desired, blowing agents

f) and also, if desired, further auxiliaries and/or additives.

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The present invention further relates to the tough polyurethane integral foams produced by this process and also to their use as beer barrel cladding.

30 The production of tough polyurethane integral foams by reacting organic polyisocyanates and/or modified organic polyisocyanates with relatively high-functionality compounds containing at least two reactive hydrogen atoms and, if desired, low molecular weight chain extenders and/or crosslinkers in the presence of catalysts,
35 blowing agents, auxiliaries and/or additives is known and has been described many times. A summary overview of the production of polyurethane integral foams is given, for example, in the Kunststoff-Handbuch, Volume VII, "Polyurethane", 1st Edition 1966, edited by Dr. R. Vieweg and Dr. A. Höchtlen, and 3rd Edition 1993,
40 edited by Becker/Braun (Carl Hanser Verlag, Munich).

It is likewise known that polyurethane foams can be produced using polyols which in turn have been obtained from polyurethane waste by reaction with compounds containing at least 2 OH groups,
45 known as glycolysis. Thus, for example, DE-A-25 16 863 describes the preparation of a polyol mixture from polyurethane waste and aliphatic diols, which mixture is suitable for the production of

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rigid polyurethane foams. According to DE-A-40 24 601, glycolysis of polyurethane-urea waste gives a polyol-containing dispersion which can be used for producing rigid or semirigid polyurethanes or polyurethane-ureas. According to US 4,014,809 (DE-A-25 57 172),
5 polyol-containing liquid mixtures synthesized from rigid polyurethane foams are reused as rigid foam components. Polyol-containing liquids prepared as described in DE-A-37 02 495 from polyurethane waste are described as being suitable for semirigid and rigid polyurethanes, in particular polyurethane
10 foams.

The recycled polyols prepared by the known processes always contain the amines which are also formed in the glycolysis and are hazardous to health and furthermore have an adverse effect on
15 the polyurethane systems formulated from the recycled polyols. They strongly accelerate the polyurethane formation reaction, form rigid urea groups and reduce the controllability of the polyurethane formation reaction by means of other catalysts. Furthermore, the content of free amines in polyol components of
20 polyurethane systems immediately leads, on contact with isocyanates, to highly thixotropic masses, as described in DD-A-156 480.

A variety of processes has become known for the purpose of
25 deamination. The recycled polyol deaminated as described in DE-A-40 24 601 by addition of monomeric acrylic acid has an acid number of significantly above 1 mg KOH/g, which can lead to difficulties in the polyurethane systems containing the recycled polyol. Furthermore, the distinct acrylic acid odor is a problem.
30 According to DE-A-44 16 322, low molecular weight ureas and/or carbamic esters can also be used for the deamination. EP-A-0 592 952 describes the use of glycidyl ethers for preparing recycled polyols which are low in amines.

35 The recycled polyols obtained in this way are used for producing semirigid and rigid polyurethane foams. The documents do not suggest an improvement in the quality of the polyurethane foams resulting from the use of these recycled polyols. Only DE-A-44 11 864 indicates that the use of recycled polyol prepared
40 by glycolysis of flexible foam waste using glycidyl ethers enables rigid polyurethane foams having an increased proportion of open cells and reduced shrinkage to be produced.

High demands are placed on the mechanical properties of tough
45 polyurethane integral foams. Apart from the formation of particular cell structures, the foams are required to achieve a demanding level of mechanical properties. Particularly important

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here are very high tear propagation resistance, elongation at break and tensile strength, particularly when, as is the case, for example, for beer barrel cladding, strong external forces act on the polyurethane material.

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It is an object of the present invention to develop a simple and inexpensive process for producing tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength.

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We have found that this object is achieved by producing the tough polyurethane integral foams using a recycled polyol which is obtained by glycolysis of tough polyurethane integral foams using glycidyl ethers.

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The present invention accordingly provides a process for producing tough polyurethane integral foams having improved tear propagation resistance, elongation at break and tensile strength by reacting

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- a) organic and/or modified organic polyisocyanates with
- b) at least one relatively high molecular weight compound containing at least two reactive hydrogen atoms and, if
25 desired,
- c) low molecular weight chain extenders and/or crosslinkers
in the presence of
- 30 d) catalysts,
- e) if desired, blowing agents

35 f) and also, if desired, further auxiliaries and/or additives,

wherein the component b) used comprises at least one recycled polyol which is obtained by glycolysis of tough polyurethane integral foams using glycidyl ethers.

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The present invention further provides the tough polyurethane integral foams produced by this process and also provides for their use as beer barrel cladding.

45 It is surprising and was in no way foreseeable that the use of recycled polyols prepared from tough polyurethane integral foams by glycolysis again gives high-quality tough polyurethane

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integral foams which have improved tear propagation resistance, elongation at break and tensile strength. Rather, it would have been expected that the mechanical properties of the foam would be worsened by use of recycled polyols.

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An economical process for producing tough polyurethane integral foams which are very suitable for beer barrel cladding has thus been found.

- 10 According to the present invention, relatively high molecular weight compounds containing at least two reactive hydrogen atoms which are used are completely or partially recycled polyols either alone or in admixture with one another. For achieving the desired mechanical properties, recycled polyols are
- 15 advantageously used in a proportion of at least 30 % by weight, based on the total amount of the component b). For economic reasons, the amount of recycled polyol used can be substantially above 30 % by weight or the component b) can consist entirely of recycled polyol. Naturally, less than 30 % by weight of recycled
- 20 polyols can also be used.

- The recycled polyols are obtained by glycolysis of tough polyurethane integral foams, in particular their waste, using short-chain, hydroxyl-containing compounds such as ethylene
- 25 glycol, diethylene glycol, triethylene glycol, oligoethylene glycols, propylene glycol, dipropylene glycol, tripropylene glycol, oligopropylene glycols, butanediols, neopentyl glycol, glycerol, ethanolamine, diethanolamine and triethanolamine, in the presence or absence of catalysts such as alkali metal salts
- 30 of short-chain fatty acids, titanates, stannates and antimonates at elevated temperatures. "

- Tough polyurethane integral foams used are, in particular, polyurethane waste as is obtained, for example, particularly in
- 35 the production of beer barrel cladding; these can contain, inter alia, fillers or reinforcers which do not interfere in the process.

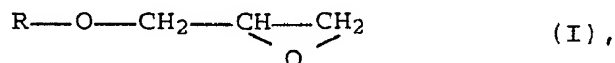
- The recycled polyols used according to the present invention are
- 40 preferably low in amines. They are obtainable, in particular, by carrying out the glycolysis of the polyurethane integral foams while metering in monofunctional and/or difunctional glycidyl ethers during the entire course of the reaction, as is described in EP-A-0 592 952.

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In the preparation of the recycled polyols, it is possible to use commercial glycidyl ethers which have one or two epoxide groups in the molecule.

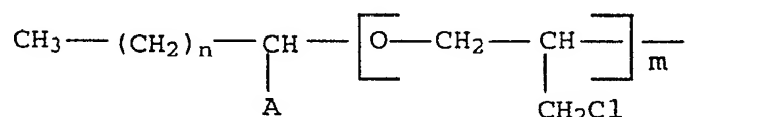
- 5 Glycidyl ethers which have been found to be particularly useful are the monofunctional glycidyl ethers of the formula (I)



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where R = phenyl, cyclohexyl, methylcyclohexyl, benzyl, i-propyl, i-butyl or methyl and/or ethyl-branched hydrocarbon chains having from 5 to 10 carbon atoms in the straight chain and/or a group of the formula

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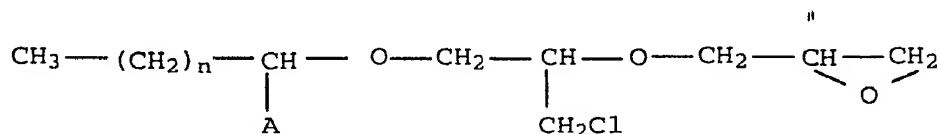
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where A is an alkyl radical having from 1 to 8 carbon atoms, n is from 3 to 12 and m is from 1 to 6.

- 25 Preference is given to using 2-ethylhexyl glycidyl ether or a mixture of

from 50 to 85 % by weight of 2-ethylhexyl glycidyl ether, from 10 to 35 % by weight of one or more compounds having the structure

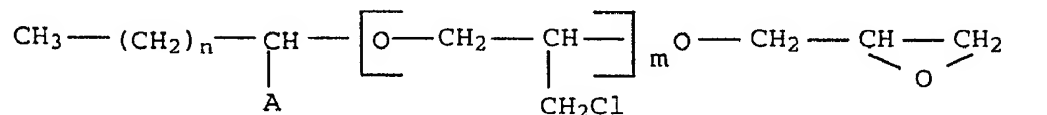
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35 and

from 5 to 20 % by weight of one or more compounds having the structure

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- 45 where A is an alkyl radical having from 1 to 8 carbon atoms, n is from 3 to 12 and m is from 2 to 6. This glycidyl ether mixture can be prepared in a known manner from 2-ethylhexanol and epichlorohydrin as is obtained in the synthesis of 2-ethylhexyl

2-methylpentamethylene 1,5-diisocyanate, tetramethylene 1,4-diisocyanate and preferably hexamethylene 1,6-diisocyanate; cycloaliphatic diisocyanates such as cyclohexane 1,3- and 1,4-diisocyanate and also any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), hexahydrotolylene 2,4- and 2,6-diisocyanate and also the corresponding isomer mixtures, dicyclohexylmethane 4,4'-, 2,2'- and 2,4'-diisocyanate and also the corresponding isomer mixtures, and preferably aromatic diisocyanates and polyisocyanates such as tolylene 2,4- and 2,6-diisocyanate and the corresponding isomer mixtures, diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanate and the corresponding isomer mixtures, mixtures of diphenylmethane 4,4'- and 2,4'-diisocyanates, polyphenylpolymethylene polyisocyanates, mixtures of diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanates and polyphenylpolymethylene polyisocyanates (raw MDI) and mixtures of raw MDI and tolylene diisocyanates. The organic diisocyanates and polyisocyanates can be used individually or in the form of their mixtures.

Use is frequently also made of modified polyfunctional isocyanates, ie. products which are obtained by chemical reaction of organic diisocyanates and/or polyisocyanates. Examples which may be mentioned are diisocyanates and/or polyisocyanates containing ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione and/or urethane groups. Specific examples of suitable modified isocyanates are: organic, preferably aromatic polyisocyanates containing urethane groups, having NCO contents of from 33.6 to 15 % by weight, preferably from 31 to 21 % by weight, based on the total weight, and prepared, for example, by reaction with low molecular weight diols, triols, dialkylene glycols, trialkylene glycols or polyoxyalkylene glycols having molecular weights of up to 6000, in particular up to 1500, modified diphenylmethane 4,4'-diisocyanate, modified diphenylmethane 4,4'- and 2,4'-diisocyanate mixtures, or modified raw MDI or tolylene 2,4- or 2,6-diisocyanate, with examples of dialkylene or polyoxyalkylene glycols which can be used individually or as mixtures being: diethylene glycol, dipropylene glycol, polyoxyethylene, polyoxypropylene and polyoxypropylene-polyoxyethylene glycols, triols and/or tetrols. Also suitable are prepolymers containing NCO groups, having NCO contents of from 30 to 15 % by weight, preferably from 28 to 20 % by weight, based on the total weight, and prepared from the polyester and/or preferably polyether

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polyols described below and diphenylmethane 4,4'-diisocyanate, mixtures of diphenylmethane 2,4'- and 4,4'-diisocyanate, tolylene 2,4- and/or 2,6-diisocyanates or raw MDI. Other modified polyisocyanates which have been found to be useful are liquid polyisocyanates containing carbodiimide groups and/or isocyanurate rings and having NCO contents of from 33.6 to 15 % by weight, preferably from 31 to 21 % by weight, based on the total weight, for example those based on diphenylmethane 4,4'-, 2,4'- and/or 2,2'-diisocyanate and/or tolylene 2,4- and/or 2,6-diisocyanate.

The modified polyisocyanates can, if desired, be mixed with one another or with unmodified organic polyisocyanates such as diphenylmethane 2,4'- and/or 4,4'-diisocyanate, raw MDI, tolylene 2,4- and/or 2,6-diisocyanate.

Organic polyisocyanates which have been found to be particularly useful and are therefore preferably employed are the following aromatic polyisocyanates: raw MDI, mixtures of tolylene diisocyanates and raw MDI or mixtures of modified organic polyisocyanates containing urethane groups and having an NCO content of from 33.6 to 15 % by weight, in particular those based on tolylene diisocyanates, diphenylmethane 4,4'-diisocyanate, diphenylmethane diisocyanate isomer mixtures or raw MDI and, in particular, raw MDI having a diphenylmethane diisocyanate isomer content of from 30 to 80 % by weight, preferably from 30 to 55 % by weight.

b) As relatively high molecular weight compounds containing at least two reactive hydrogen atoms, use is made, according to the present invention, of the above-described recycled polyols. In addition thereto, further relatively high molecular weight compounds containing at least two reactive hydrogen atoms (b) can be concomitantly used. Compounds suitable for this purpose are advantageously those having a functionality of from 2 to 8, preferably from 2 to 6, and a molecular weight of from 1000 to 8000, preferably from 1200 to 6000. Compounds which have been found to be useful are, for example, polyetherpolyamines and/or preferably polyols selected from the group consisting of polyether polyols, polyester polyols, polythioether polyols, polyesteramides, hydroxyl-containing polyacetals and hydroxyl-containing aliphatic polycarbonates or mixtures of at least two of the polyols mentioned. Preference is given to using polyester polyols and/or polyether polyols. The hydroxyl number of the

polyhydroxyl compounds is generally from 25 to 850 and preferably from 300 to 750.

- Suitable polyester polyols can be prepared, for example, from organic dicarboxylic acids having from 2 to 12 carbon atoms, preferably aliphatic dicarboxylic acids having from 4 to 6 carbon atoms, and polyhydric alcohols, preferably diols, having from 2 to 12 carbon atoms, preferably from 2 to 6 carbon atoms. Examples of suitable dicarboxylic acids are: succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids can be used either individually or in admixture with one another. In place of the free dicarboxylic acids, it is also possible to use the corresponding dicarboxylic acid derivatives such as dicarboxylic esters of alcohols having from 1 to 4 carbon atoms or dicarboxylic anhydrides. Preference is given to using dicarboxylic acids mixtures of succinic, glutaric and adipic acid in weight ratios of, for example, 20-35 : 35-50 : 20-32, and in particular adipic acid. Examples of dihydric and polyhydric alcohols, in particular diols, are: ethanediol, diethylene glycol, 1,2- or 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerol and trimethylolpropane. Preference is given to using ethanediol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol or mixtures of at least two of the diols mentioned, in particular mixtures of 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol. It is also possible to use polyester polyols derived from lactones, eg. ϵ -caprolactone, or hydroxycarboxylic acids, eg. ω -hydroxycaproic acid.
- To prepare the polyester polyols, the organic, eg. aromatic and preferably aliphatic, polycarboxylic acids and/or derivatives and polyhydric alcohols can be polycondensed in the absence of catalysts or preferably in the presence of esterification catalysts, advantageously in an atmosphere of inert gas such as nitrogen, carbon dioxide, helium, argon etc, in the melt at from 150 to 250°C, preferably from 180 to 220°C, under atmospheric pressure or reduced pressure to the desired acid number which is advantageously less than 10, preferably less than 2. According to a preferred embodiment, the esterification mixture is polycondensed at the abovementioned temperatures to an acid number of from 80 to 30, preferably from 40 to 30, under atmospheric pressure and

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subsequently under a pressure of less than 500 mbar, preferably from 50 to 150 mbar. Suitable esterification catalysts are, for example, iron, cadmium, cobalt, lead, zinc, antimony, magnesium, titanium and tin catalysts in the form of metals, metal oxides or metal salts. However, the polycondensation can also be carried out in the liquid phase in the presence of diluents and/or entrainers such as benzene, toluene, xylene or chlorobenzene to azeotropically distill off the water of condensation.

To prepare the polyester polyols, the organic polycarboxylic acids and/or derivatives and polyhydric alcohols are advantageously polycondensed in a molar ratio of 1:1-1.8, preferably 1:1.05-1.2.

The polyester polyols obtained preferably have a functionality of from 2 to 4, in particular from 2 to 3, and a molecular weight of from 480 to 3000, preferably from 1200 to 3000 and in particular from 1800 to 2500.

However, polyols which are particularly preferably used are polyether polyols which are prepared by known methods, for example from one or more alkylene oxides having from 2 to 4 carbon atoms in the alkylene radical by anionic polymerization using alkyl metal hydroxides such as sodium or potassium hydroxide or alkali metal alkoxides such as sodium methoxide, sodium or potassium ethoxide or potassium isopropoxide as catalysts with addition of at least one initiator molecule containing from 2 to 8, preferably from 2 to 6, reactive hydrogen atoms in bonded form, or by cationic polymerization using Lewis acids such as antimony pentachloride, boron fluoride etherate, etc., or bleaching earth as catalysts.

Suitable alkylene oxides are, for example, tetrahydrofuran, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, styrene oxide and preferably ethylene oxide and 1,2-propylene oxide. The alkylene oxides can be used individually, alternately in succession or as mixtures. Examples of suitable initiator molecules are: water, organic dicarboxylic acids, such as succinic acid, adipic acid, phthalic acid and terephthalic acid, aliphatic and aromatic, unalkylated, N-monoalkylated, N,N- and N,N'-dialkylated diamines having from 1 to 4 carbon atoms in the alkyl radical, for example unalkylated, monoalkylated or dialkylated ethylenediamine, diethylenetriamine, triethylenetetramine, 1,3-propylenediamine, 1,3- or 1,4-butylenediamine, 1,2-,

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1,3-, 1,4-, 1,5- and 1,6-hexamethylenediamine, phenylenediamines, 2,3-, 2,4- and 2,6-tolylenediamine and 4,4'-, 2,4'- and 2,2'-diaminodiphenylmethane.

5 Other suitable initiator molecules are: alkanolamines such as ethanolamine, N-methylethanolamine and N-ethylethanolamine, dialkanolamines such as diethanolamine, N-methyldiethanolamine and N-ethyldiethanolamine, and trialkanolamines such as triethanolamine, and ammonia.
10 Preference is given to using polyhydric, in particular dihydric and/or trihydric alcohols such as ethanediol, 1,2- and 1,3-propanediol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, aerythritol, sorbitol and sucrose.

15 The polyether polyols, preferably polyoxypropylene and polyoxypropylene-polyoxyethylene-polyols, have a functionality of preferably from 2 to 6 and in particular from 2 to 4 and molecular weights of from 1000 to 8000,
20 preferably from 1200 to 6000 and in particular from 1800 to 4000, and suitable polyoxytetramethylene glycols have a molecular weight up to about 3500.

25 Further suitable polyether polyols are polymer-modified polyether polyols, preferably graft polyether polyols, in particular those based on styrene and/or acrylonitrile which are prepared by in situ polymerization of acrylonitrile, styrene or preferably mixtures of styrene and acrylonitrile, eg. in a weight ratio of from 90 : 10 to 10 : 90, preferably
30 from 70 : 30 to 30 : 70, advantageously in the abovementioned polyether polyols using methods similar to those described in the German Patents 11 11 394, 12 22 669 (US 3 304 273, 3 383 351, 3 523 093), 11 52 536 (GB 10 40 452) and 11 52 537 (GB 987 618), and also polyether polyol dispersions which
35 contain as dispersed phase, usually in an amount of from 1 to 50 % by weight, preferably from 2 to 25 % by weight: eg. polyureas, polyhydrazides, polyurethanes containing bonded tert-amino groups and/or melamine and are described, for example, in EP-B-011 752 (US 4 304 708), US 4 374 209 and
40 DE-A-32 31 497.

Like the polyether polyols, the polyether polyols can be used individually or in the form of mixtures. They can also be mixed with the graft polyether polyols or polyester polyols
45 as well as with the hydroxyl-containing polyesteramides, polyacetals, polycarbonates and/or polyetherpolyamines.

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Suitable hydroxyl-containing polyacetals are, for example, the compounds which can be prepared from glycols such as diethylene glycol, triethylene glycol, 4,4'-dihydroxyethoxydiphenyldimethylmethane or hexanediol and formaldehyde. Suitable polyacetals can also be prepared by polymerization cyclic acetals.

Suitable hydroxyl-containing polycarbonates are those of the type known per se, which can be prepared, for example, by reacting diols such as 1,3-propanediol, 1,4-butanediol and/or 1,6-hexanediol, diethylene glycol, triethylene glycol or tetraethylene glycol with diaryl carbonates, eg. diphenyl carbonate, or phosgene.

The polyesteramides include, for example, the predominantly linear condensates obtained from polybasic, saturated and/or unsaturated carboxylic acids or their anhydrides and polyfunctional saturated and/or unsaturated aminoalcohols or mixtures of polyfunctional alcohols and aminoalcohols and/or polyamines.

Suitable polyetherpolyamines can be prepared from the abovementioned polyether polyols by known methods. Examples which may be mentioned are the cyanoalkylation of polyoxyalkylene polyols and subsequent hydrogenation of the nitrile formed (US 3 267 050) or the partial or complete amination of polyoxyalkylene polyols using amines or ammonia in the presence of hydrogen and catalysts (DE 12 15 373).

c) The elastic polyurethane integral foams can be produced with or without use of chain extenders and/or crosslinkers (c). However, the use of chain extenders, crosslinkers or, if desired, mixtures thereof can prove to be advantageous for modifying the mechanical properties, eg. the hardness. Chain extenders and/or crosslinkers used are diols and/or triols having molecular weights of less than 400, preferably from 60 to 300. Suitable chain extenders/crosslinkers are, for example, aliphatic, cycloaliphatic or araliphatic diols having from 2 to 14, preferably from 4 to 10, carbon atoms, for example ethylene glycol, 1,3-propanediol, 1,10-decanediol, o-, m-, p-dihydroxycyclohexane, diethylene glycol, dipropylene glycol and preferably 1,4-butanediol, 1,6-hexanediol and bis(2-hydroxyethyl)hydroquinone, triols such as 1,2,4- or 1,3,5-trihydroxycyclohexane, glycerol and trimethylolpropane and low molecular weight hydroxyl-containing polyalkylene oxides based on ethylene

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oxide and/or 1,2-propylene oxide and the abovementioned diols and/or triols as initiator molecules.

- 5 If chain extenders, crosslinkers or mixtures thereof are employed for producing the polyurethane integral foams, they are advantageously used in an amount of from 0 to 20 % by weight, preferably from 2 to 8 % by weight, based on the weight of the polyol compound (b).
- 10 d) Catalysts (d) used for producing the tough polyurethane integral foams are, in particular, compounds which strongly accelerate the reaction of the compounds containing reactive hydrogen atoms, in particular hydroxyl groups, of the component (b) and, if used, (c) with the organic, modified or
- 15 unmodified polyisocyanates (a). Suitable catalysts are organic metal compounds, preferably organic tin compounds such as tin(II) salts of organic carboxylic acids, eg. tin(II) acetate, tin(II) octoate, tin(II) ethylhexoate and tin(II) laurate, and the dialkyltin(IV) salts of organic
- 20 carboxylic acids, eg. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate. The organic metal compounds are used alone or preferably in combination with strongly basic amines. Examples are amidines such as 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, tertiary amines such as triethylamine, tributylamine, dimethylbenzylamine, N-methylmorpholine, N-ethylmorpholine, N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutanediamine, N,N,N',N'-tetramethylhexane-1,6-diamine, pentamethyldiethylenetriamine,
- 25 bis(dimethylaminoethyl) ether, bis(dimethylaminopropyl)urea, dimethylpiperazine, 1,2-dimethylimidazole, 1-azabicyclo[3.3.0]octane and preferably 1,4-diazabicyclo[2.2.2]octane, and alkanolamine compounds such as triethanolamine, triisopropanolamine,
- 30 N-methyldiethanolamine and N-ethyldiethanolamine and dimethylethanolamine.
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Further suitable catalysts are:

- 40 tris(dialkylaminoalkyl)-s-hexahydrotriazines, in particular tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetraalkylammonium hydroxides such as tetramethylammonium hydroxide, alkali metal hydroxides such as sodium hydroxide and alkali metal alkoxides such as sodium methoxide and potassium isopropoxide, and also alkali metal salts of
- 45 long-chain fatty acids having from 10 to 20 carbon atoms and possibly lateral OH groups. Preference is given to using from 0.001 to 5 % by weight, in particular from 0.05 to 2 % by

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weight, of catalyst or catalyst combination, based on the weight of the component (b).

- 5 e) Blowing agents (e) which may, if desired, be used for producing the polyurethane integral foams include preferably water which reacts with isocyanate groups to form carbon dioxide. The amounts of water which are advantageously used are from 0.1 to 8 parts by weight, preferably from 1.5 to 10 5.0 parts by weight and in particular from 0.5 to 2.0 parts by weight, based on 100 parts by weight of the polyoxyalkylene polyols.

- 15 In admixture with water, it is also possible to use physically acting blowing agents. Suitable physically acting blowing agents are liquids which are inert toward the organic, modified or unmodified polyisocyanates (c) and have boiling points below 100°C, preferably below 50°C, in particular from -50°C to 30°C, at atmospheric pressure, so that they vaporize under the action of the exothermic 20 polyaddition reaction. Examples of such preferred liquids are alkanes such as heptane, hexane, n- and iso-pentane, preferably industrial mixtures of n- and iso-pentanes, n- and iso-butane and propane, cycloalkanes such as cyclopentane and/or cyclohexane, ethers such as furan, dimethyl ether and 25 diethyl ether, ketones such as acetone and methyl ethyl ketone, alkyl carboxylates such as methyl formate, dimethyl oxalate and ethyl acetate and halogenated hydrocarbons such as methylene chloride, dichloromonofluoromethane, difluoromethane, trifluoromethane, difluoroethane, 30 tetrafluoroethane, chlorodifluoroethanes, " 1,1-dichloro-2,2,2-trifluoroethane, 2,2-dichloro-2-fluoroethane and heptafluoropropane. Mixtures of these low-boiling liquids with one another and/or with other substituted or unsubstituted hydrocarbons can also be 35 used. Also suitable are organic carboxylic acids such as formic acid, acetic acid, oxalic acid, ricinoleic acid and carboxyl-containing compounds.

- 40 Preference is given to using water, chlorodifluoromethane, chlorodifluoroethanes, dichlorofluoroethanes, pentane mixtures, cyclohexane and mixtures of at least two of these, eg. mixtures of water and cyclohexane, mixtures of chlorodifluoromethane and 1-chloro-2,2-difluoroethane and, if 45 desired, water.

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- f) If desired, auxiliaries and/or additives (f) customary in polyurethane chemistry can also be incorporated into the reaction mixture for producing the tough polyurethane integral foams. Examples which may be mentioned are foam stabilizers, fillers, dyes, pigments, flame retardants, hydrolysis inhibitors, fungistatic and bacteriostatic substances.

For the purposes of the present invention, fillers, in particular reinforcing fillers, are the customary organic and inorganic fillers, reinforcers, weighting agents, agents for improving the abrasion behavior in paints, coating compositions, etc., known per se. Specific examples are: inorganic fillers such as siliceous minerals, for example sheet silicates such as antigorite, serpentine, hornblends, amphiboles, chrysotile, talc; metal oxides such as kaolin, aluminum oxides, titanium oxides and iron oxides, metal salts such as chalk, barite and inorganic pigments such as cadmium sulfide, zinc sulfide and also glass, etc. Preference is given to using kaolin (china clay), aluminum silicate and coprecipitates of barium sulfate and aluminum silicate and also natural and synthetic fibrous minerals such as wollastonite, metal and in particular glass fibers of various lengths which may be coated with a size. Suitable organic fillers are, for example: carbon, melamine, rosin, cyclopentadienyl resins and graft polymers, and also cellulose fibers, polyamide, polyacrylonitrile, polyurethane and polyester fibers based on aromatic and/or aliphatic dicarboxylic esters and, in particular, carbon fibers.

Suitable flame retardants are, for example, tricresyl phosphate, tris(2-chloroethyl) phosphate, tris(2-chloropropyl) phosphate, tris(1,3-dichloropropyl) phosphate, tris(2,3-dibromopropyl) phosphate, tetrakis(2-chloroethyl)ethylene diphosphate, dimethyl methanephosphonate, diethyl diethanolaminomethylphosphonate and also commercial halogen-containing flame retardant polyols.

Apart from the abovementioned halogen-substituted phosphates, it is also possible to use inorganic or organic flame retardants such as red phosphorus, hydrated aluminum oxide, antimony trioxide, arsenic oxide, ammonium polyphosphate and calcium sulfate, expanded graphite or cyanuric acid derivatives such as melamine, or mixtures of at least two flame retardants such as ammonium polyphosphates and melamine and also, if desired, maize starch or ammonium polyphosphate,

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melamine and expanded graphite and/or aromatic or aliphatic polyesters for making the polyisocyanate polyaddition products flame resistance. In general, it has been found to be advantageous to use from 5 to 50 parts by weight, preferably from 5 to 25 parts by weight, of the flame retardants mentioned per 100 parts by weight of the component (b).

Further details regarding the abovementioned other customary auxiliaries and additives may be found in the specialist literature, for example the monograph by J.H. Saunders and K.C. Frisch "High Polymers", Volume XVI, Polyurethanes, Parts 1 and 2, Interscience Publishers 1962 and 1964, or the Kunststoff-Handbuch, Polyurethane, Volume VII, Hanser-Verlag, Munich, Vienna, 1st, 2nd and 3rd Editions, 1966, 1983 and 1993.

To produce the tough polyurethane integral foams, the organic polyisocyanates (a), relatively high molecular weight compounds containing at least two reactive hydrogen atoms (b) and, if desired, chain extenders and/or crosslinkers (c) are reacted in such amounts that the equivalence ratio of NCO groups of the polyisocyanates (a) to the sum of the reactive hydrogen atoms of the component (b) and, if used, (c) is preferably 0.9-1.15:1.

The tough polyurethane integral foams are advantageously produced by the one-shot process or prepolymer process by means of the high-pressure or low-pressure technique in open or closed molds, for example metal molds, or are free-foamed (in-situ foam). It has been found to be particularly advantageous to employ the two-component process and to combine the formative components (b), (d) and, if desired, (c), (e) and (f) as the component (A) and to use the organic and/or modified organic polyisocyanates (a) or mixtures of said polyisocyanates and, if desired, blowing agents (d).

The starting components are mixed at from 15 to 90°C, preferably from 20 to 60°C and in particular from 20 to 35°C, and, in the case of the production of molded foams, introduced into the open or closed mold. The mold temperature is advantageously from 20 to 110°C, preferably from 30 to 60°C and in particular from 45 to 50°C.

The tough polyurethane integral foams produced by the process of the present invention have a density of from 600 to 1,100 kg/m³,

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preferably from 700 to 800 kg/m³. They have a cellular core and a compacted surface zone.

The tough polyurethane integral foams of the present invention
5 have

a tear propagation resistance of at least 22 N/mm, preferably from 22 to 26 N/mm, determined in accordance with DIN 53507,

10 an elongation at break of at least 27 %, preferably from 27 to 50 %, determined in accordance with DIN 53504, and

a tensile strength of at least 6.8 N/mm², preferably from 6.8 to 8.0 N/mm², determined in accordance with DIN 53504.

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The tough polyurethane integral foams produced by the process of the present invention are suitable for all customary applications for tough polyurethane integral foams. They are used in particular for beer barrel cladding.

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The invention is illustrated by the following examples.

Example 1 (Comparative Example):

25 A Component

Mixture of:

- 63.51 parts by weight of a glycerol-initiated
30 polyoxypropylene-polyoxyethylene polyol having an OHN of 35 mg KOH/g,
9.6 parts by weight of a propylene glycol-initiated
polyoxypropylene-polyoxyethylene polyol having an OHN of 29 mg KOH/g,
35 17.95 parts by weight of an ethylenediamine-initiated
polyoxypropylene polyol having an OHN of 740 mg KOH/g,
0.98 part by weight of a 33 % strength by weight solution of Dabco in dipropylene glycol,
4.86 parts by weight of tris(2-chloroisopropyl) phosphate
40 (TCPP),
0.5 part by weight of water and
2.60 parts by weight of color paste

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B Component:

Prepolymer containing urethane groups, having an NCO content of 28 % and prepared by reacting diphenylmethane diisocyanate/
5 polyisocyanate with a propylene glycol-initiated polyoxypropylene polyol having an OHN of 250 mg KOH/g.

100 parts by weight of the A component were reacted with 53 parts by weight of the B component, giving a tough integral foam having
10 the following properties:

Density of molding [kg/m ³]:	710
Hardness [Shore D]:	40
Tensile strength [N/mm ²]:	6.6
15 Elongation at break [%]:	26.9
Tear propagation resistance [N/mm]:	21.1

Example 2 (Preparation of the recycled polyol)

20 2000 g of tough integral foam waste (beer barrel cladding) were introduced at 205°C into a mixture of 1000 g of diethylene glycol (DEG) and 0.1 % by weight of tin(II) octoate (based on DEG and polyurethane waste) in such a way that the contents of the flask remained stirrable. This temperature was maintained for 2.5 hours
25 while stirring. During the reaction time, 12 % by weight of 2-ethylhexyl glycidyl ether (based on amount of DEG and polyurethane waste) was uniformly metered in.

The mixture was subsequently cooled to 150°C, 3 % by weight of
30 2-ethylhexyl glycidyl ether was metered in and the mixture was reacted at this temperature for 0.5 hour. This gave a homogeneous black liquid having the following properties:

OHN	370 mg KOH/g
35 AN	< 0.1 mg KOH/g
Viscosity	5280 mPa.s
MDA content	< 0.1 %

Example 3

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A Component

Mixture of:

45 30 parts by weight of recycled polyol prepared as described in Example 2 from integral foam waste (beer barrel cladding) and having an OHN of 370 mg KOH/g,

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- 52.40 parts by weight of a glycerol-initiated polyoxypropylene-polyoxyethylene polyol having an OHN of 35 mg KOH/g,
- 10.20 parts by weight of a propylene glycol-initiated polyoxypropylene-polyoxyethylene polyol having an OHN of 29 mg KOH/g,
- 5 6.0 parts by weight of an ethylenediamine-initiated polyoxypropylene polyol having an OHN of 740 mg KOH/g,
- 0.90 part by weight of a 33 % strength by weight solution of Dabco in dipropylene glycol and
- 10 0.5 part by weight of water.

B Component: As in Example 1

- 15 100 parts by weight of the A component were reacted with 57.3 parts by weight of the B component, giving a tough integral foam having the following properties:

Density of molding [kg/m ³]:	730
20 Hardness [Shore D]:	39
Tensile strength [N/mm ²]:	7.9
Elongation at break [%]:	32.4
Tear propagation resistance [N/mm]:	25.1

25 Example 4

A Component

Mixture of:

- 30
- 39 parts by weight of recycled polyol prepared as described in Example 2 from integral foam waste (beer barrel cladding) and having an OHN of 370 mg KOH/g,
- 48.9 parts by weight of a glycerol-initiated polyoxypropylene-polyoxyethylene polyol having an OHN of 35 mg KOH/g,
- 35 10.7 parts by weight of a propylene glycol-initiated polyoxypropylene-polyoxyethylene polyol having an OHN of 29 mg KOH/g,
- 40 0.9 part by weight of a 33 % strength by weight solution of Dabco in dipropylene glycol and
- 0.5 part by weight of water.

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B Component: As described in Example 1

100 parts by weight of the A component were reacted with 54 parts by weight of the B component, giving a tough integral foam having 5 the following properties:

Density of molding [kg/m ³]:	700
Hardness [Shore D]:	41
Tensile strength [N/mm ²]:	7.0
10 Elongation at break [%]:	49.6
Tear propagation resistance [N/mm]:	23.8

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We claim:

1. A process for producing tough polyurethane integral foams ha-
5 ving improved tear propagation resistance, elongation at
break and tensile strength by reacting
 - a) organic and/or modified organic polyisocyanates with
 - 10 b) at least one relatively high molecular weight compound
containing at least two reactive hydrogen atoms and, if
desired,
 - c) low molecular weight chain extenders and/or crosslinkers
15 in the presence of
 - d) catalysts,
 - 20 e) if desired, blowing agents
 - f) and also, if desired, further auxiliaries and/or additi-
ves,
- 25 wherein the component b) used comprises at least one recycled
polyol which is obtained by glycolysis of tough polyurethane
integral foams using glycidyl ethers.
2. A process as claimed in claim 1, wherein the recycled polyol
30 is used in a proportion of at least 30 % by weight, based on
the total amount of the component b).
3. A process as claimed in claim 1, wherein monofunctional and/
or difunctional glycidyl ethers are used in the preparation
35 of the recycled polyols.
4. A process as claimed in claim 1, wherein the recycled polyol
used is low in amines.
- 40 5. A tough polyurethane integral foam having improved tear pro-
pagation resistance, elongation at break and tensile strength
obtainable by reacting
 - a) organic and/or modified organic polyisocyanates with
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- b) at least one relatively high molecular weight compound containing at least two reactive hydrogen atoms and, if desired,
- 5 c) low molecular weight chain extenders and/or crosslinkers in the presence of
- d) catalysts,
- 10 e) if desired, blowing agents
- f) and also, if desired, further auxiliaries and/or additives,
- 15 wherein the component b) used comprises at least one recycled polyol which is obtained by glycolysis of tough polyurethane integral foams using glycidyl ethers.
- 20 6. A tough polyurethane integral foam as claimed in claim 5, wherein the recycled polyol is used in a proportion of at least 30 % by weight, based on the total amount of the component b).
- 25 7. A tough polyurethane integral foam as claimed in claim 5 which has a tear propagation resistance of at least 22 N/mm².
8. A tough polyurethane integral foam as claimed in claim 5 which has an elongation at break of at least 27 %.
- 30 9. A tough polyurethane integral foam as claimed in claim 5 which has a tensile strength of at least 6.8 N/mm².
10. Use of a tough polyurethane integral foam as claimed in claim 5 as beer barrel cladding.
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